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ELECTRICAL CONDUCTIVITY OF ANODE SUPPORTED NiO-BCZY|BCZY|LSCF-BCZY BUTTON CELL AT INTERMEDIATE TEMPERATURES

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ABSTRACT

In this study, the NiO-BCZY anode, BCZY ($BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$) electrolyte, and LSCF($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$)-BCZY cathode powder were synthesized using a sol gel technique. NiO-BCZY anode supported button cell was fabricated with some modification on the fabrication processes of electrolyte and cathode layers. Both of the electrolyte and cathode powders were made into slurries and separately spin coated on the anode pellet to form single cell of NiO-BCZY|BCZY|LSCF-BCZY. Electrical measurement of the cell was carried out using an electrochemical impedance spectroscopy (EIS) and its microstructure was observed using a scanning electron microscopy (SEM). The area specific resistance (ASR) and conductivity (σ) of the single cell at operating temperature of 750 ^{o}C is 17.78 Ω cm^2 and 4.44 $\times 10^{-3}$ S cm^{-1}, respectively. The SEM result shows the electrolyte thin film was well adhered on the anode substrate as no delamination was observed between anode-electrolyte and electrolyte-cathode interface, respectively. The activation energy (E_a) of the cell calculated from the Arrhenius plot was 0.51 eV.

Keywords: PCFC; NiO-BCZY anode; button cell

INTRODUCTION

Nowadays, researchers are moving towards producing clean and efficient energy sources that are sustainable and renewable. The solid oxide fuel cells (SOFCs) is one of the energy sources that are actively developed by the engineers and researchers world-wide. The SOFCs have a great potential to be the most efficient, versatile technology and low environmental pollution [1]. They can be divided into two types based on their electrolyte species which are conventional SOFCs (oxide ion conductor, O^{2-}-SOFC) and

proton conducting SOFCs (PCFC or H^+-SOFC). The typical electrolyte material that has been used for conventional SOFCs is a yttria stabilized zirconia (YSZ), and for PCFC is a yttrium doped barium cerium-zirconium oxide (BCZY). Traditionally, conventional SOFCs operate at higher operating temperature which are 800 ^oC to 1000 ^oC. In order to reduce the high operating temperature, many novels of modified SOFCs are being introduced such as proton conducting fuel cells (PCFCs) with thin film electrolyte. In addition, the use of thin film electrolyte will reduce the ohmic resistance of the cell in producing high energy of PCFC at temperature in the range of 400-800 ^oC [2].

Thus, the overall performance of anode supported button cell consisting of NiO-$BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ (BCZY) as anode material, BCZY as electrolyte and LSCF($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$)-BCZY as cathode material was studied in this work. Both electrolyte and cathode layers were improvised by layering the electrolyte on anode pellet. The cathode composite of LSCF-BCZY was spin coated on the electrolyte component. The thermal mismatch between electrolyte-cathode layer can be reduced by using cathode composite compared with pure cathode, and eventually can reduce the possibility of delamination between electrolyte and cathode layers [3]. The electrochemical performance of the fabricated anode button cell was carried out using an electrochemical impedance spectroscopy (EIS) under fuel cell condition.

EXPERIMENTAL

Preparation of powder and slurries

A stoichiometric amount of barium nitrate, cerium (III) nitrate hexahydrate, zirconyl (IV) nitrate hydrate, and yttrium (III) nitrate hexahydrate, were firstly weighted and dissolved in 150 ml deionized water. Next, the citric acid monohydrate (CA) and ethylenediaminetetraacetic acid (EDTA) were added in the metal nitrates solution and stirred for 24 h. Then the ethylene glycol (EG) was gradually added and the pH of the solution was adjusted using ammonium hydroxide until the pH of the solutions about 7.0 ± 0.5 under continuously stirring. The homogenized solution was simultaneously heated and stirred at 120-220 °C for several hours. The product in the form of viscous gel was dried using a hotplate at 325°C. Lastly, it was pre-calcined at 325°C for 2 h using CarboliteTM Furnace chamber and formed sponge-like solid. The solid sample was grinded and then calcined at 1100 °C for 10 h to obtain BCZY fine yellow powder [4]. In order to produce BCZY electrolyte slurry, the BCZY powder was mixed with binder. The binder was made by mixing ethyl cellulose and terpineol, and the electrolyte slurry was obtained by mixing 0.5 g of BCZY powder with the binder, stirred for 30 min and then dispersed in an ultrasonic bath for another 30 min. Furthermore, to produce LSCF-BCZY cathode slurry, 0.6 g of LSCF-BCZY powder was mixed with prepared binder and the mixture was subjected for dispersion process using ultrasonic bath. Details preparation of LSCF powder was reported elsewhere [5].

Fabrication of single cell

Fabrication of anode supported button cell was firstly done by a dry pressing technique on the anode side and then spin coating technique at respective electrolyte and cathode layers. An approppriate amount of NiO-BCZY powder was pressed into pellet with 13 mm diameter and sintered at 1400 °C. Then, electrolyte and cathode slurries were spin coated onto the anode pellet. Two step sintering (TSS) process at temperature of 1500 °C (1 min) and 1450 °C for 6 h was performed to sinter anode-electrolyte layer. A complete single cell (anode, electrolyte, and cathode layers) was also sintered also using TSS with temperature of 600 °C (1 h) and 950 °C (3 h) to form NiO-BCZY|BCZY|LSCF-BCZY button cell.

Characterization of the single cell

The microstructure and electrical measurements of the single cell was carried-out using a scanning electron microscopy (SEM) and an electrochemical impedance spectroscopy (EIS), respectively. The resistivity and electrical conductivity of the anode supported button cell were measured at intermediate temperature in the range of 400 °C to 800 °C under fuel cell condition. The single cell was reduced in humidified hydrogen (10% H_2) for three hours. Impedance data was collected in open circuit voltage (OCV) condition with frequency range of 0.1Hz to 1MHz, using ZIVE SP2 Electrochemical Workstation (ZIVE LAB WonATech) Electrochemical Workstation assisted with personal computer.

RESULTS AND DISCUSSION

Figure 1 shows the impedance plots of the anode supported button cell measured at 650, 700, and 750 °C, respectively. The arc in the impedance spectrum represents the electrical signals that can be associated to the electrodes and electrolyte responses. There were two significant arcs observed in each of the impedance spectrum. At high frequency intercept, the arc represents the ohmic resistance, R_o (resistance of the electrolyte thin film), and the total resistance of the cell (R_t) at the low frequency intercept. The difference between R_t and R_o was the polarization resistance, R_p (resistance of the electrodes). In order to verify the responses were belong to the electrodes or electrolyte signal, the capacitance of the cell was calculated using :

$$C = Y^{\frac{1}{n}} * R^{\frac{1}{n}-1} \quad \ldots\ldots\ldots \quad (1)$$

where C is the capacitance, (F), Y is the quantity in the block diagram, (Q_y), R is the resistance for each arc, (Ω), (R1 and R2) and N is the quantity in the block diagram (Q_a)

The capacitance values of the cell obtained at 750 °C for arc 1 and arc 2 were 3.08×10^{-6} F and 1.36×10^{-2} F, respectively indicating that the responses corresponded to the electrodes counterpart. These capacitance values were eventually obtained from the fitting procedure using an equivalent circuit based on Brick-layer model. They were matched to the respond of the single cell as the response of the electrodes must be in the

range of 10^{-2} to 10^{-6} F [5].

The larger impedance arc was observed at 650 °C showing that the polarization resistance (R_p) was the highest among all the three temperatures. However, as the temperature increased, the polarization as well as ohmic resistance (R_o) decreased indicating that the tested button cell belongs to a class of thermally activated process. The area specific resistance (ASR) calculated for the temperature of 650 °C, 700 °C and 750 °C was 30.44, 23.14, and 17.78 Ωcm^2, respectively.

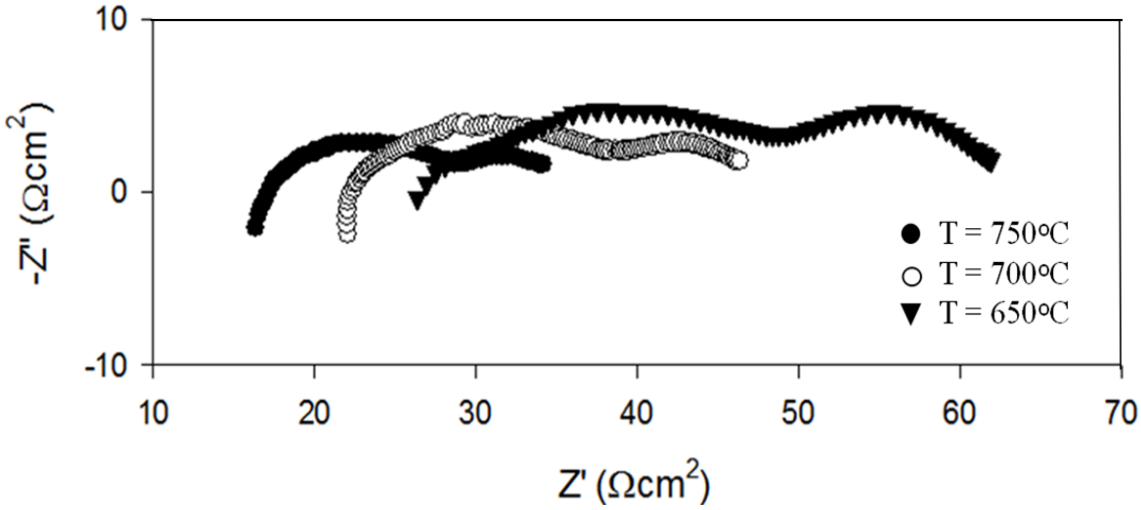

Figure 1: Impedance plots of NiO-BCZY anode supported button cell in fuel-cell condition
(10% H_2 + 90% N_2 : air) at different temperatures

The total conductivity of the cell were 2.63×10^{-3}, 3.46×10^{-3}, and 4.49×10^{-3} S cm^{-1} at 650, 700 and 750 °C, respectively as calculated using Equation 2:

$$\sigma = \frac{t}{RA} \quad \ldots\ldots\ldots (2)$$

where σ is the conductivity, (S/cm), A is the area of electrode, (cm^2), t is the thickness, (cm) and R is the resistivity, (Ω)

Figure 2 presents the Arrhenius plot of the single cell. The activation energy (E_a) of the single cell was 0.51 eV and the obtained value was comparable to the study performed by Ranran et al. which was 0.45 eV [7].

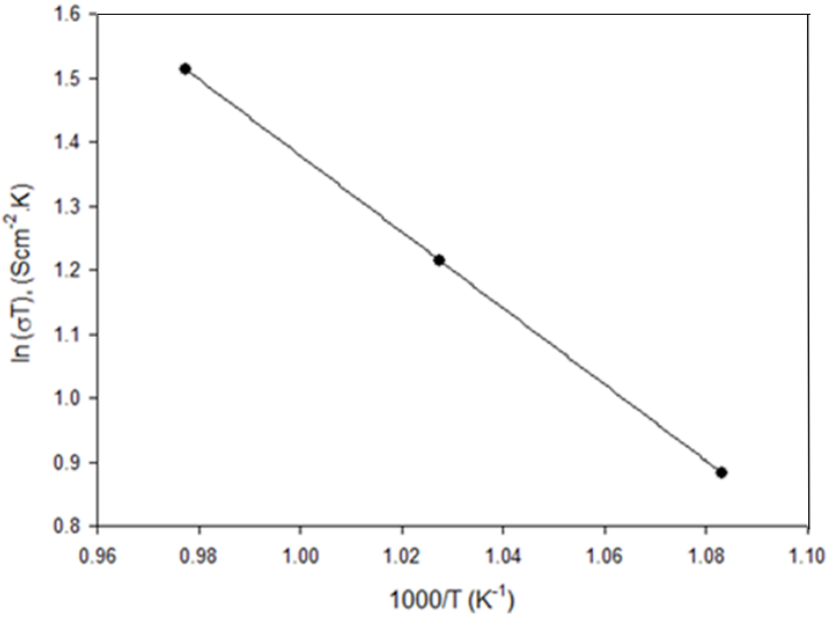

Figure 2: Arrhenius plot of the single cell measured at three different temperatures

The SEM micrographs of the cross-sectional single cell and electrolyte layer re presented in Figure 3(a) and Figure 3(b), respectively. The image showed that the electrolyte thin film was firmly deposited on the anode layer without any delamination occurred at the interfacial of anode-electrolyte layer as well as electrolyte-cathode layer. However, clearly seen in Figure 3(b), the electrolyte layer was not well densified and exhibited larger grains size. These observations may contribute to the high ohmic resistance (R_o) as well as ASR values that caused to the lower performance of the button cell. It is crucial for the BCZY electrolyte thin film to be denser in order to optimize the mobility of ion hydrogen (H^+) from anode to cathode layer [2]. Thus, modification and improvement of the electrolyte part will become our main concern in future work.

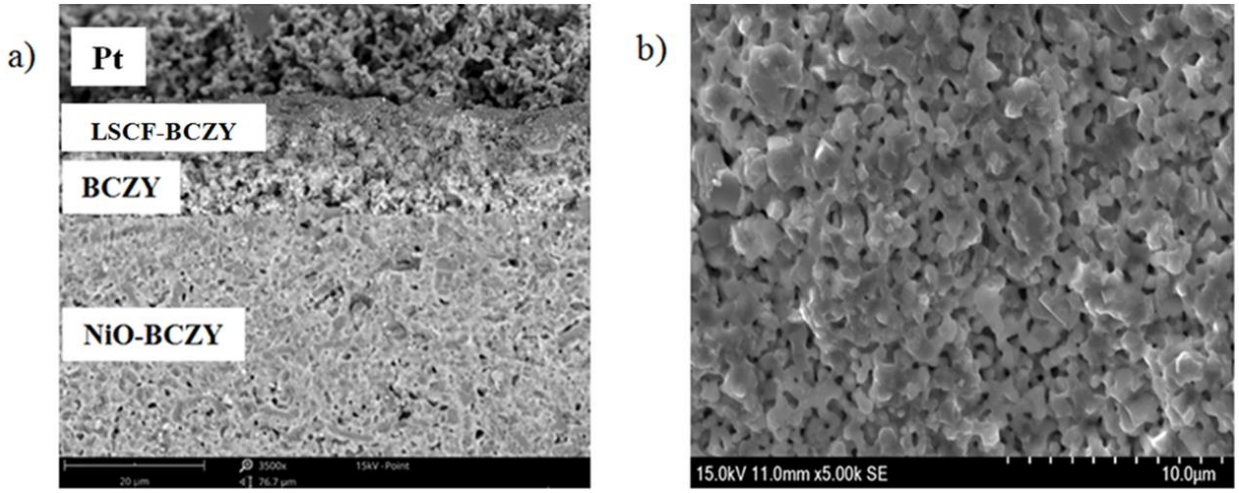

Figure 3: SEM micrographs of the cross-sectional view of (a) single cell and (b) electrolyte layer

CONCLUSIONS

The NiO-BCZY anode supported button cell was fabricated using a dry pressing and spin coating techniques. Resistance of the single cell was higher compared with other studies possibly due to the lower density of the electrolyte layer. Thus, further material modifications such as addition of sintering aid or surfactant is needed to obtain dense electrolyte thin film. The dense thin film will contribute to low ohmic resistance and can reduce the polarization resistance as well to enhance the overall performance of the single cell.

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